INORG. NUCL. CHEM. LETTERS Vol. 5, pp. 337-338, 1969. Pergamon Press. Printed in Great Britain.

ON THE STRUCTURE OF AgO

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(Received 23 January 1969)

The silver oxide AgO has been first considered as a silver(I) peroxide, and until recent years as a silver (II) oxide. The absence of peroxide properties and the diamagnetic behaviour are not in accordance with either assumptions. It was also proposed the existence of a bond between both silver atoms of AgO, in order to explain its diamagnetism.

Neutron diffraction studies of Scatturin and coworkers (1) confirmed the statement of McMillan (2) about the existence of two kinds of silver atoms in AgO.

According to these results, the formula of this silver oxide may be represented by:

$$Ag^{I}[Ag^{III}O_2] \quad \text{or} \quad Ag^{I}-O-Ag^{III}=O$$

The authors (3) intended to find by means of isotopic exchange a difference in the behaviour of silver atoms of AgO. After exchange with $^{*}Ag^{+}_{(aq)}$, they tried to separate the two differents atoms of the AgO. No chemical method has been published to distinguish or to separate the Ag(I) and Ag(III) of the AgO, so the authors looked for one. It was found that the separation is possible by reacting AgO with KIO_4 in strong alkaline media at 30 °C. A well known silver(III) complex is produced according to the following chemical equation:

$$4\ AgO + 6\ KOH + 4\ KIO_4 = 2K_5H_2[Ag(IO_6)_2] + Ag_2O + H_2O.$$

This reaction can be used:

1) as a method to separate Ag(III) from Ag(I) in AgO.
2) as a chemical evidence of the existence of two non-equivalent silver atoms in AgO.
3) as a new method to prepare silver(III) periodates.

In the present comunication, the authors also report that a similar reaction can be carried out with potassium tellurate, as follows:

$$4\ AgO + 6KOH + 4\ K_2TeO_4 = 2\ K_7H_2Ag(TeO_6)_2 + Ag_2O + H_2O.$$

Isotopic exchange in both homogeneous and heterogeneous phases between the AgO and $Ag(IO_6)_2^{7-}$ or $Na_5H_2Ag(IO_6)_2$ species allowed the authors to demonstrate that the silver(III) complex was formed via the $Ag(OH)_4^-$ ion produced by partial dissolution of AgO in basic media without involving a redox process between AgO and KIO_4.

Studying the stoichiometry of these reactions, it was found that more Ag_2O is formed owing to the partial decomposition of AgO in concentrated KOH solution. In blank tests with AgO and KOH the amount of Ag_2O formed by decomposition corresponds to that found in excess in the former tests.

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